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Growth of Dense Vertical and Horizontal Graphene for Thermal Vias and its Thermal Property

Akio Kawabata, Tomo Murakami, Mizuhisa Nihei and Naoki Yokoyama
Collaborative Research Team Green Nanoelectronics Center (GNC)
National Institute of Advanced Industrial Science and Technology (AIST)
West 7A, Onogawa 16-1, Tsukuba, Ibaraki 305-8569, Japan
Phone: +81-29-849-1487 e-mail: kawabata.akio@aist.go.jp

1. Introduction

Carbon nanotubes, graphene and other nanocarbon materials hold promise for applications in electronics because of their unique electrical [1-2] and thermal characteristics [3]. The known electrical characteristics include ballistic transport of carrier conduction along the tube, and tolerance for high density. The application of those electrical characteristics to LSI via interconnects have been reported previously [4-6]. There are also a number of reports on the thermal characteristics, however, large gaps remain between their ideal properties and the experimental data, particularly due to the issues that relate to CNT density factors [7-11].

There are some reports on high-density CNT structures. MIRAI-Selete group has reported CNT densities of over 10^{12} /cm^2 [12-13]. In this study, we report a previously unseen dense vertical and horizontal graphene (DVHG) structure, in which vertical graphene layers were formed densely below horizontal graphene layers, perpendicular to the substrate. We also tried to measure the thermal characteristics of DVHG structures by picosecond thermoreflectance measurement [14].

2. Experimental

The experiments were conducted with a newly-developed multi-chamber process that is capable of substrate pre-processing, catalyst metal deposition and nanocarbon thermal CVD growth in vacuum batch. The base vacuum pressure is 3.0 x 10^{-5} Pa.

We deposited TaN (15 nm thick) layer on the SiOC dielectric/Si substrate having via holes with a diameter of 160 nm in SiOC dielectric layer. The substrate is subjected to Ar plasma etching in the pre-processing chamber to very slightly etch the TaN surface. Next, Ti (1 nm thick) and Co (4 nm thick) are deposited in the vacuum vapor deposition chamber. The substrate is then moved to the thermal CVD chamber, where it is heated to the growth temperature of 450°C in vacuum. After that, a mixture of acetylene and argon gas is introduced to the gas pressure of 1kPa. The growth time is 30 minutes.

3. Results and Discussion

A high-resolution SEM (Scanning Electron Microscope) observation revealed that the columnar carbon structure was obtained after the growth in via holes, as shown in Fig. 1a. The surface is flat and appears like a mirror to the eye. A cross-section TEM (Transmission Electron Microscope) observation confirmed the contrast in the columnar carbon structure. Looking at the entire cross-section image, the contrast is confirmed in the lower part and in the middle of part of the structure, that may be the catalyst metal, but none is observed in the upper part. A magnified view of the lower part (Fig. 1b) clearly confirms the contrast of graphene formed in the direction perpendicular to the substrate. And a magnified view of the upper part (Fig. 1c) confirms that the horizontal graphene layer about 2-nm thick has been formed. What is notable here is that no empty structures are seen in the CNT (Fig. 1d), and nearly all vertical graphene is formed. From that fact, we know that there is horizontal graphene in the upper part of the structure and vertical graphene in the lower part, which is a structure that has not been seen previously. Figure 1e shows the illustration describing the DVHG structure obtained in this study. A CNT/graphene structure in which the uppermost part is graphene was reported by Kondo *et al.* [15], but the structure reported here features the formation of vertical graphene at high density in the CNT part.

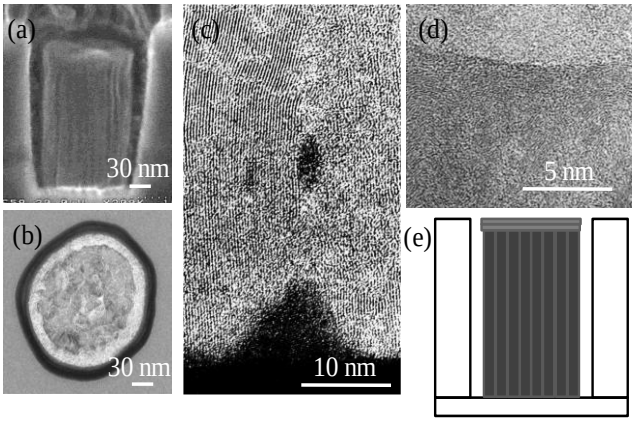

Fig. 1 DVHG structure observed by (a) SEM, (b) parallel -section TEM, and magnified (c) the lower part and (d) the upper part. (e) Schematic of DVHG structure.

The density of that structure determined by calculations from X-ray reflectivity measurements shows an extremely high value of 1.4 g/cm^3. That is denser by a factor of 2.4 than the 0.57 g/cm^3 of high-density packed SWNT reported by Futaba *et al.* [16] and is 63% of the 2.2 g/cm^3 of graphite. We consider this to be applicable as a new method of forming high density nanocarbon materials.

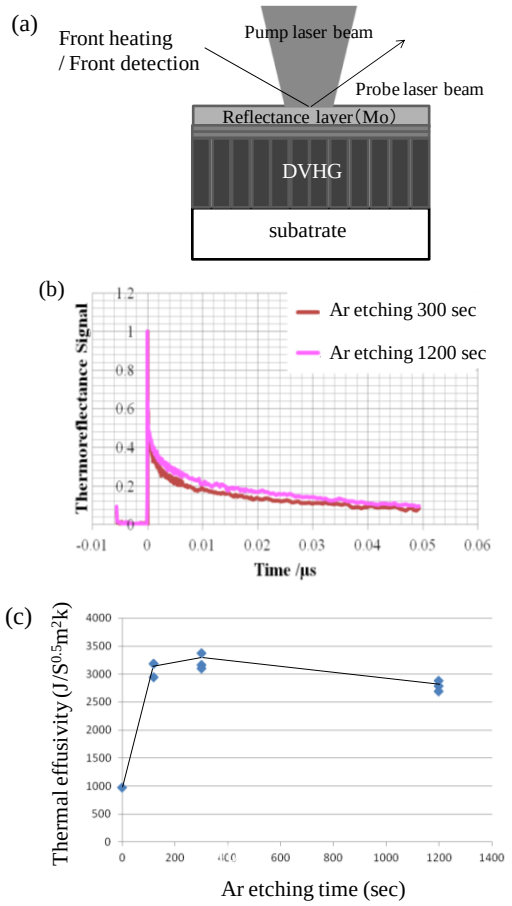

Fig. 2 (a) Picosecond thermoreflectance measurement system. (b) Thermoreflectance signal. (c) Ar etching time vs. Thermal effusivity.

We measured the thermal characteristics with a picosecond thermoreflectance measurement system (PicoTherm Corporation). The measurement method, which is referred to as pulse optical heating thermoreflectance, involves the formation of a Mo thin-film (reference) on the object to be measured and the measurement of the thermal effusivity of the material beneath the Mo thin-film from the reflectance of the heated Mo surface (Fig. 2a).

The thermal effusivity and thermal conductivity are related as expressed by the following equation.

$$b = \sqrt{\lambda c \rho}$$

b: thermal effusivity ρ: density
λ: thermal conductivity c: specific heat capacity

What is important in this measurement is the reflection of laser light by the Mo surface, so the surface of the object to be measured must be flat. Because the surface of the structure obtained in this work consists of horizontal graphene at the upper part, the surface remains flat after formation of the Mo layer and measurement is possible. Because horizontal graphene forms the surface of this structure, we do not expect the thermal effusion to proceed directly to the vertical structure. For that reason, we introduced the process of Ar plasma etching is performed in the pre-processing chamber to remove the horizontal graphene. The etching times were 120 seconds, 300 seconds, and 1200 seconds. As an example, the measured signals for the case with the etching time of 300 and 1200 seconds are shown in Fig. 2b.

As shown in Fig. 2c, with no etching, the thermal effusivity was 975 $J/S^{0.5}m^2k$, the lowest value for any of the measurement conditions. An improvement was seen in the thermal effusivity for all of the etching conditions. The most improvement was obtained with the etching time of 300 seconds, for which the thermal effusivity was 3162 $J/S^{0.5}m^2k$. Using a density value of 1.4 g/cm^3 and the specific heat value 710 kJ/kgK of graphite [17, 18], we obtained the thermal conductivity values of 1.0 W/mK and 10 W/mK for the case with no etching and the etching time of 300 seconds, respectively. As expected, we can improve the thermal conductivity by removing the horizontal graphene on the vertical graphene structure. In order to improve its thermal conductivity further, we are now trying to higher quality vertical graphene structure by applying higher temperature growth conditions.

4. Conclusions

We demonstrate the DVHG structure fabricated by the vacuum batch multi-chamber process. And we determined the thermal characteristics of DVHG by picosecond thermoreflectance measurement. The value was 1.0 W/mK with the horizontal graphene exists and 10 W/mK with the horizontal graphene removed.

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